

(19) World Intellectual Property Organization  
International Bureau(43) International Publication Date  
31 January 2008 (31.01.2008)

PCT

(10) International Publication Number  
**WO 2008/013518 A1**

## (51) International Patent Classification:

C22B 34/12 (2006.01) C22C 14/00 (2006.01)  
C22C 1/04 (2006.01)

## (21) International Application Number:

PCT/US2006/028396

(22) International Filing Date: 22 July 2006 (22.07.2006)

(25) Filing Language: English

(26) Publication Language: English

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125 South Wacker Drive, Suite 2080, Chicago, IL 60606  
(US).(81) Designated States (unless otherwise indicated, for every  
kind of national protection available): AE, AG, AL, AM,AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,  
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,  
GB, GD, GE, GH, GM, HN, HR, HU, ID, IL, IN, IS, JP,  
KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT,  
LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA,  
NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC,  
SD, SE, SG, SK, SL, SM, SJ, TJ, TM, TN, TR, TT, TZ,  
UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.(84) Designated States (unless otherwise indicated, for every  
kind of regional protection available): ARIPO (BW, GH,  
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,  
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),  
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,  
FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT,  
RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA,  
GN, GQ, GW, ML, MR, NE, SN, TD, TG).

## Published:

- with international search report
- the filing date of the international application is within two months from the date of expiration of the priority period
- with information concerning one or more priority claims considered void

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: TITANIUM ALLOY

(57) Abstract: A titanium base alloy powder having lesser amounts of aluminum and vanadium with an alkali or alkaline earth metal being present in an amount of less than about 200 ppm. The alloy powder is neither spherical nor angular and flake shaped. 6/4 alloy is specifically disclosed having a packing fraction or tap density between 4 and 11 %, as is a method for making the various alloys.



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## **TITANIUM ALLOY**

### **FIELD OF THE INVENTION**

This invention relates to alloys of titanium having at least 50% titanium and most specifically to an alloy of titanium particularly useful in the aerospace and defense industries known as 6/4 which is about 6% by weight aluminum and about 4% by weight vanadium with the balance titanium and trace materials as made by the Armstrong process.

### **BACKGROUND OF THE INVENTION**

The ASTM B265 grade 5 chemical specifications for 6/4 require that vanadium is present in the amount of  $4\% \pm 1\%$  by weight and aluminum is present in the range of from about 5.5 % to about 6.75 % by weight. The alloy of the invention is produced by the Armstrong Process as previously disclosed in U.S. patent nos. 5,779,761; 5,958,106 and 6,609,797, the entire disclosures of which are herein incorporated by reference. The aforementioned patents teach the Armstrong Process as it relates to the production of various materials including alloys. The Armstrong Process includes the subsurface reduction of halides by a molten metal alkali or alkaline earth element or alloy. The development of the Armstrong Process has occurred from 1994 through the present, particularly as it relates to the production of titanium and its alloys using titanium tetrachloride as a source of titanium and using sodium as the reducing agent. Although this invention is described particularly with respect to titanium tetrachloride, aluminum trichloride and vanadium tetrachloride and sodium as a reducing metal, it should be understood that various halides other than chlorine can be used and various reductants other than sodium can be used and the invention is broad enough to include those materials.

However, because the Armstrong Process over the past eleven years has been developed using molten sodium and chlorides, it is these materials which are referenced herein. During the production of titanium by the Armstrong Process, as disclosed in the previous patents, the steady state temperature of the reaction can be controlled by the amount of reductant metal and the amount of chloride being introduced. Although it is feasible to control the reaction temperature by varying the chloride concentration while keeping the amount of molten metal constant, the

preferred method is to control the temperature of the reactant products by varying the amount of excess (over stoichiometric) reductant metal introduced into the reaction chamber. Preferably, the reaction is maintained at a steady state temperature of about 400°C and at this temperature, as previously disclosed, the reaction can be maintained for very long periods of time without damage to the equipment while producing a relatively uniform product.

Heretofore, commercially pure (CP) titanium ASTM B265 grades 1, 2, 3 and 4 have been produced in over two hundred runs using the Armstrong Process and although a wide variety of operating parameters have been tested, certain results are inherent in the process. The ASTM B 265 spec sheet follows:

TABLE 1 - Chemical Requirements

Element	Composition %									
	Grade									
	1	2	3	4	5	6	7	8	9	10
Nitrogen max	0.03	0.03	0.05	0.05	0.05	0.05	0.03	0.02	0.03	0.03
Carbon max	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.08
Hydrogen <sup>a</sup> max	0.015	0.015	0.015	0.015	0.015	0.020	0.015	0.015	0.015	0.015
Iron Max <sup>b</sup>	0.30	0.30	0.50	0.40	0.50	0.30	0.25	0.20	0.30	
Oxygen max	0.18	0.25	0.35	0.40	0.20	0.20	0.25	0.15	0.18	0.25
Aluminum	...	...	...	...	5.5 to 6.75	4.0 to 8.0	...	2.5 to 3.5	...	...
Vanadium	...	...	...	...	3.5 to 4.5	...	...	2.0 to 3.0	...	...
Tin	...	...	...	...	...	2.0 to 3.0	...	...	...	...
Palladium	...	...	...	...	...	...	0.12 to 0.25	...	0.12 to 0.25	...
Molybdenum	...	...	...	...	...	...	...	...	...	0.2 to 0.4
Zirconium	...	...	...	...	...	...	...	...	...	...
Nickel	...	...	...	...	...	...	...	...	...	0.6 to 0.9
Residuals <sup>c,d,e</sup>	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
(each), max										
Residuals <sup>c,d,e</sup>	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
(total) max										
Titanium <sup>f</sup>	remainder	remainder	remainder	remainder	remainder	remainder	remainder	remainder	remainder	remainder

<sup>a</sup> Analysis shall be completed for all elements listed in this Table for each grade. The analysis results for the elements not quantified in the Table need not be reported unless the concentration level is greater than 0.1% each or 0.4% total.

<sup>b</sup> Lower hydrogen may be obtained by negotiation with the manufacturer.

<sup>c</sup> Need not be reported.

<sup>d</sup> A residual is an element present in a metal or an alloy in small quantities inherent to the manufacturing process but not added intentionally.

<sup>e</sup> The purchaser may, in his written purchase order, request analysis for specific residual elements not listed in this specification. The maximum allowable concentration for residual elements shall be 0.1% each and 0.4% maximum total.

<sup>f</sup> The percentage of titanium is determined by difference.

Production of titanium powder by the Armstrong Process inherently produces powder in which the average diameter of an individual particle is less than a micron. During distillation at 500 to 600°C, the particles agglomerate and have an average agglomerated particle diameter in the range of from about 3.3 to about 1.3 microns. Particle diameters are based on a calculated size of a sphere from a surface area, such as BET. For agglomerated particles, the calculated average diameters were based on surface area measurements in a range of from about 0.4 to about 1.0 m<sup>2</sup> per gram. In over two hundred runs, the titanium powder produced by the Armstrong Process always has a packing fraction in the range of from about 4% to about 11% which also may also be expressed as tap density. Tap density is a well known characteristic and is determined by introducing the powder into a graduated test tube and tapping the tube until the powder is fully settled. Thereafter, the weight of the powder is measured and the packing fraction or percent of theoretical density is calculated.

Moreover, during the production of CP titanium by the Armstrong Process, a certain amount of sodium has always been retained even after extensive distillation, including vacuum distillation, and this retained sodium has been present on average of about 500 - 700 ppm, and has rarely been below about 400 ppm. From a commercial point of view, significant effort is and has been expended in order to reduce the sodium content of CP titanium made by the Armstrong Process.

Prior to the Armstrong Process, CP titanium powder and titanium alloy powder traditionally have been made by two methods, hydride-dehydride and spheridization, resulting in powders having very different morphologies than the powder made by the Armstrong method. Hydride-dehydride powders are angular and flake-like, while spheridized powders are spheres.

Fines made during the Hunter process are available and these also have very different morphology than CP titanium produced by the Armstrong Process. SEMs of CP powder made by the hydride-dehydride process and the spheridization process and Hunter fines are illustrated in Figs. 1 to 3, respectively. The CP powder made by the Armstrong Process is not spherical nor is it angular and flake-like. Hunter fines have "large inclusions" which do not appear in the Armstrong powder, differentiating Figs. 1-3 from Armstrong powder shown in Figs. 4 - 9. Moreover, Hunter fines have

large concentrations of chlorine while Armstrong CP powder has low concentrations of chlorine; chlorine is an undesirable contaminant.

6/4 powder is made by hydride-dehydride and spherization processes, but not by the Hunter process. A calcium reduction hydride-dehydride process used in Tula, Russia was identified by Moxson et al. in an article in The International Journal Of Powder Metallurgy, Vol. 34, No. 5, 1998. Moxson et al which also discloses SEMs of both CP and 6/4 in the Journal Of Metallurgy, May, 2000, both articles, the disclosures of which are incorporated by reference, taken together showing that 6/4 powder made by methods other than the Armstrong process result in powders that are very different from Armstrong 6/4 powder, both in size distribution and/or morphology and/or chemistry. In some cases, such as the calcium reduction process in Tula, Russia there are very significant differences in chemistry as well as the other differences previously mentioned. Both the hydride -dehydride and spherization methods require Ti, Al and V to be mixed as liquids and thereafter formed into powder. Only the Armstrong Process produces alloy powder directly from gas mixtures of the alloy constituents.

Because 6/4 titanium is the most common titanium alloy used by the Department of Defense (DOD) as well as the aerospace industry and other significant industries, the production of 6/4 by the Armstrong Process is an important commercial goal.

#### **SUMMARY OF THE INVENTION**

Accordingly, a principal object of the present invention is to provide a titanium base alloy powder having lesser amounts of aluminum and vanadium with unique morphological and chemical properties.

Another object of the present invention to provide a titanium base alloy powder having about 6 percent by weight aluminum and about 4 percent by weight vanadium within current ASTM specifications.

Yet another object of the invention is to make a 6/4 alloy as set forth in which sodium is present in significantly smaller amounts than is present in CP titanium powder made by the Armstrong Process.

Still another object of the present invention is to provide a titanium base alloy powder having about 6% by weight aluminum and about 4% by weight vanadium with

an alkali or alkaline earth metal being present in an amount less than about 200 ppm and the alloy powder being neither spherical nor angular or flake shaped.

A further object of the present invention is to provide a titanium base alloy powder having about 6% by weight aluminum and about 4% by weight vanadium with an alkali or alkaline earth metal being present in an amount less than about 200 ppm and having a tap density or packing fraction in the range of from about 4% to about 11%.

Yet another object of the present invention is to provide a titanium base alloy powder having about 6% by weight aluminum and about 4% by weight vanadium with an alkali or an alkaline earth metal being present in an amount less than about 200 ppm made by the subsurface reduction of chloride vapor with molten alkali metal or molten alkaline earth metal.

A final object of the present invention is to provide an agglomerated titanium base alloy powder having about 6% by weight aluminum and about 4% by weight vanadium with an alkali or alkaline earth metal being present in an amount less than about 100 ppm substantially as seen in the SEMs of Figs. 10-12.

The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and particularly pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

For the purpose of facilitating an understanding of the invention, there is illustrated in the accompanying drawings a preferred embodiment thereof, from an inspection of which, when considered in connection with the following description, the invention, its construction and operation, and many of its advantages should be readily understood and appreciated.

FIGURE 1 is a SEM of CP powder made by the hydride-dehydride method;

FIG. 2 is a SEM of CP powder made by the spheridization method;

FIG. 3 is a SEM of CP powder from the Hunter Process;

FIGS. 4-6 are SEMs of Armstrong CP distilled, dried and passivated;

FIGS. 7-9 are SEMs of Armstrong CP distilled, dried, passivated and held at

750°C for 48 hours; and

FIGS. 10-12 are SEMs of Armstrong 6/4 distilled, dried, passivated and held at 750°C for 48 hours.

#### DETAILED DESCRIPTION OF THE INVENTION

As used herein, a "titanium base alloy" means any alloy having 50% or more by weight titanium. Although 6/4 is used as a specific example, other titanium base alloys are included in this invention. As seen from the previous discussion, Armstrong CP titanium powder is different from spheridized titanium powder and from hydride-dehydride titanium powder in both morphology and packing fraction or tap density. There are also differences in certain of the chemical constituents. For instance, Armstrong CP titanium powder has sodium present in the 400 - 700 ppm range while spheridized and hydride-dehydride powder should have none or only trace amounts. Armstrong CP titanium has little chloride concentration, on the order of <50 ppm, while Hunter fines have much larger concentrations of chlorides, on the order of 0.12 - 0.15 wt. %.

The equipment used to produce the 6/4 alloy is substantially as disclosed in the aforementioned patents disclosing the Armstrong Process with the exception that instead of only having a titanium tetrachloride boiler 22 as illustrated in those patents, there is also a vanadium tetrachloride boiler and an aluminum trichloride boiler which are connected to the reaction chamber by suitable valves. The piping acts as a manifold so that the gases are completely mixed as they enter the reaction chamber and are introduced subsurface to the flowing liquid sodium. It was determined during production of the 6/4 alloy that aluminum trichloride is corrosive and required special materials not required for handling either titanium tetrachloride or vanadium tetrachloride. Therefore, Hastelloy C-276 was used for the aluminum trichloride boiler and the piping to the reaction chamber.

During most of the runs the steady state temperature of the reactor was maintained at about 400°C by the use of sufficient excess sodium. Other operating conditions for the production of the alloy were as follows:

A device similar to that described in the incorporated Armstrong patents was used except that a  $\text{VCl}_4$  boiler and  $\text{AlCl}_3$  boiler were provided and both gases were fed into the line feeding  $\text{TiCl}_4$  into the liquid Na. The boiler pressures and system



parameters are listed hereafter.

**Experimental Procedure:**

TiCl<sub>4</sub> Boiler Pressure = 500 kPa

VCl<sub>4</sub> Boiler Pressure = 630 kPa

AlCl<sub>3</sub> Boiler Pressure = 830 kPa

Inlet Na temperature = 240°C

Reactor Outlet Temperature = 510 C

Na Flowrate = 40 kg/min

TiCl<sub>4</sub> Flowrate = 2.6 kg/min

For this specific experiment, a 7/32" nozzle was used in the reactor to meter the mix of metal chloride vapors. A .040" nozzle was used to meter the AlCl<sub>3</sub> and a .035" nozzle was used to meter the VCl<sub>4</sub> into the TiCl<sub>4</sub> stream. The reactor was operated for approximately 250 seconds injecting approximately 11 kg of TiCl<sub>4</sub>. The salt and titanium alloy solids were captured on a wedge wire filter and free sodium metal was drained away. The product cake containing titanium alloy, sodium chloride and sodium was distilled at approximately 100 milli - torr at 550 to 575°C vessel wall temperatures for 20 hours. Once all the sodium metal was removed via distillation, the trap was re-pressurized with argon gas and heated to 750°C and held at temperature for 48 hours. The vessel containing the salt and titanium alloy cake was cooled and the cake was passivated with a 0.7 wt % oxygen/argon mixture. After passivation, the cake was washed with deionized water and subsequently dried in a vacuum oven at less than 100°C.

Table 1 below sets forth a chemical analysis of various runs for 6/4 alloy from an experimental loop running the Armstrong Process.

**TABLE 2**  
**Ti 6/4 FROM EXPERIMENTAL LOOP**

Run	Size	Oxygen	Sodium	Nitrogen	Hydrogen	Chloride	Vanadium	Aluminum	Carbon	Iron	
N-269-	*	0.187	0.019	0.006	0.0029	0.001		5.58	5.58	0.019	0.014
N-269-	+	0.113	0.0015	0.008	0.003	0.001	5.33	5.38	0.03	0.021	
N-269-	+	0.128	0.0006	0.005	0.0037	0.001		5.84	5.47	0.039	0.02
N-271-	+	0.124	0.002	0.001	0.0066	0.0016	4.87	6.95	0.033	0.037	
N-276	+	0.111	0.0018					4.44	6.04		
N-276	+	0.121	0.0018	0.005	0.0043	0.0005		4.12	6.35	0.012	0.016
N-276	+	0.131	0.0019	0.003	0.0057	0.0011		4.03	5.67	0.012	0.016
N-276	+	0.169	0.0026					4.1	6.02		
N-276	+	0.128	0.0015	0.003	0.0042	0.0005		3.8	6.02	0.012	0.019
N-277	+	0.155	0.0018	0.003	0.0053	0.0006		3.45	5.73	0.014	0.015
N-277	+	0.135	0.0023					3.49	5.49		
N-276	*	0.121	0.0041	0.005	0.0052	0.0005		4.31	6.53	0.02	0.015
N-276	*	0.134	0.0075					3.81	5.92		
N-276	*	0.175	0.014	0.012	0.0066	0.0005			3.96	6.01	
N-276	*	0.187	0.046	0.007	0.0081	0.0005			3.95	6.05	
N-277	*	0.141	0.0022	0.004	0.0038	0.0026		3.65	5.42		
mean		0.14125	0.0069125	0.0051667	0.00495	0.00095	4.295625	5.914375	0.0212222	0.0192222	
stand dev.		0.0253811	0.0116064	0.0028868	0.0015952	0.000626	0.7343838	0.4335892	0.0102808	0.0071024	

\* = BULK

+ = SMALL

As seen from the above Table 2, the sodium levels for 6/4 are very low on the order of 69 ppm and for certain runs, sodium levels have been undetectable. This result was unexpected because over two hundred runs of CP titanium have been made using the Armstrong Process, and sodium has always been present in the range of from about 400-700 ppm. Therefore, the lack of sodium in the 6/4 alloy was not only unexpected but an important consideration since sodium may adversely affect the welds of CP titanium.

Other important aspects shown in Table 2 are the percentages of vanadium and aluminum in the 6/4 showing an average of about 5.91% aluminum and about 4.29% vanadium for all of the runs. The runs reported in Table 2 were made with an experimental loop and the valving and control systems for metering the appropriate amount of both vanadium and aluminum were rudimentary. Advanced valving systems have now been installed to control more closely the amount of vanadium and aluminum in the 6/4 produced from the Armstrong Process, although even with the rudimentary control system, the 6/4 alloy was within ASTM specifications. Also of significance is the low iron and chloride content of the 6/4 alloy.

An additional unexpected feature of the 6/4 alloy compared to the CP titanium is the surface area, as determined using BET Specific Surface Area analysis with krypton as the adsorbate. In general, the specific surface area of the 6/4 alloy is much larger than the CP titanium and this also was unexpected. Surface analysis of CP particles which were distilled overnight (about 8-12 hours) between 500 - 575°C were 0.534 square meters/gram whereas 6/4 alloy measured 3.12 square meters/gram, indicating that the alloy is significantly smaller than the CP.

The SEMs show that the 6/4 powder is "frillier" than CP powder, see Figs. 4-9 and 10-12. As reported by Moxson et al., *Innovations in Titanium Powder Processing* in the

Journal of Metallurgy May 2000, it is clear that by-product fines from the Kroll or Hunter Processes contain large amounts of undesirable chlorine which is not present in the CP titanium powder made by the Armstrong Process (see Table 1). Moreover, the morphology of the Hunter and Kroll fines, as previously discussed, is different from the CP powder made by the Armstrong Process. Neither the Kroll nor the Hunter process has been adapted to produce 6/4 alloy. Alloy powders have been produced by melting prealloyed stock and thereafter using either gas atomization or a hydride-dehydride process (MHR). The Moxson et al. article discloses 6/4 powder made in Tula, Russia and as seen from Fig. 2 in that article, particularly Figures 2c and 2d the powders made by Tula Hydride Reduction process are significantly different than those made by the Armstrong Process. Moreover, referring to the Moxson et al. article in the 1998 issue of the International Journal of Powder Metallurgy, Vol. 4, No. 5, pages 45-47, it is seen that the chemical analysis for the pre-alloy 6/4 powder produced by the metal-hydride reduction (MHD) process contains exceptional amounts of calcium and also is not within ASTM specifications for aluminum.

Because the 6/4 alloy made by the Armstrong Process is made without the presence of either calcium or magnesium, these metals should be present, if at all, only in trace amounts and certainly much less than 100 ppm. Sodium which would be expected to be present in significant quantities based on the operation of the Armstrong Process to produce CP titanium in fact is present only at minium quantities in the 6/4 alloy. Specifically, sodium in the 6/4 alloy made by the Armstrong Process is almost always present less than 200 ppm and generally less than 100 ppm. In some instances, 6/4 alloy has been produced using the Armstrong Process in which sodium is undetectable so that this is a great and unexpected advantage of the 6/4 alloy *vis a vis* CP titanium made by

the Armstrong Process.

Both the Armstrong CP titanium and 6/4 alloy have tap densities or packing fractions in the range of from about 4% to 11%. This tap density or packing fraction is unique and inherent in the Armstrong Process and, while not advantageous particularly with respect to powder metallurgical processing, distinguishes the CP powder and the 6/4 powder made by the Armstrong Process from all other known powders.

As is well known in the art, solid objects can be made by forming 6/4 or CP titanium into a near net shapes and thereafter sintering, see the Moxson et al. article and can also be formed by hot isostatic pressing, laser deposition, metal injecting molding, direct powder rolling or various other well known techniques. Therefore, the titanium alloy powder made by the Armstrong method may be formed into a sintered product or may be formed into a solid object by well known methods in the art and the subject invention is intended to cover all such products made from the powder of the subject invention.

While the invention has been particularly shown and described with reference to a preferred embodiment hereof, it will be understood by those skilled in the art that several changes in form and detail may be made without departing from the spirit and scope of the invention which includes titanium base alloys having lesser amounts of aluminum and vanadium and is specifically not limited to the specific alloys disclosed.

**WE CLAIM:**

1. A titanium base alloy powder having lesser amounts of aluminum and vanadium with an alkali or alkaline earth metal being present in an amount of less than about 200 ppm and said alloy powder being neither spherical nor angular and flake shaped.

2. The titanium base alloy of claim 1, wherein the total amount of aluminum and vanadium is less than about 20% by weight.

3. The titanium alloy powder of claim 1, wherein said powder is in agglomerates having an average mean diameter as measured by sieve analysis greater than about 50 microns.

4. The titanium alloy powder of claim 1, wherein the surface area as determined by BET analysis is at least about 3 square meters per gram after distillation of the powder at temperatures between about 500°C and about 575°C for about 8 to about 12 hours.

5. The titanium alloy powder of claim 1, wherein sodium and magnesium and calcium are present in an amount of less than about 100 ppm.

6. The titanium alloy powder of claim 1, wherein the tap density is in the range of from about 4% to about 11%.

7. The titanium alloy powder of claim 1 formed into a sintered product.

8. A solid object made from the titanium alloy powder of claim 1.

9. A titanium base alloy powder having about 6% by weight aluminum and about 4% by weight vanadium with an alkali or alkaline earth metal being present in an amount of less than about 200 ppm and said alloy powder being neither spherical nor angular and flake shaped.

10. The titanium alloy powder of claim 9, wherein said powder is in agglomerates having an average mean diameter as measured by sieve analysis greater than about 50 microns.

11. The titanium alloy powder of claim 9, wherein the surface area as determined by BET analysis is at least about 3 square meters per gram after distillation of the powder at temperatures between about 500°C and about 575°C for about 8 to about 12 hours.

12. The titanium alloy powder of claim 9, wherein sodium and magnesium and calcium are present in an amount of less than about 100 ppm.

13. The titanium alloy powder of claim 9, wherein said powder meets ASTM B265 grade 5 chemical specifications.

14. The titanium alloy powder of claim 9, wherein the tap density is in the range of from about 4% to about 11%.

15. The titanium alloy powder of claim 9 agglomerated as seen in Figs. 10-12.

16. The titanium alloy powder of claim 9 formed into a sintered product.

17. A solid object made from the titanium alloy powder of claim 9.

18. A titanium base alloy powder having about 6% by weight aluminum and about 4% by weight vanadium with an alkali or alkaline earth metal being present in an amount less than about 200 ppm and having a tap density in the range of from about 4% to about 11%.

19. The titanium alloy powder of claim 18, wherein the surface area as determined by BET analysis is at least about 3 square meters per gram after distillation of the powder at temperatures between about 500°C and about 575°C for about 8 to about 12 hours.

20. The titanium alloy powder of claim 18, wherein sodium and calcium and magnesium are present in an amount of less than about 100 ppm.

21. The titanium alloy powder of claim 18, wherein said powder meets ASTM B265 grade 5 chemical specifications.

22. The titanium alloy powder of claim 18 agglomerated as seen in Figs A to B.

23. The titanium alloy powder of claim 18 formed into a sintered product.

24. A solid object made from the titanium alloy powder of claim 18.

25. A titanium base alloy powder having about 6% by weight aluminum and about 4% by weight vanadium with an alkali or an alkaline earth metal being present in an amount less than about 200 ppm made by the subsurface reduction of chloride vapor with molten alkali metal or molten alkaline earth metal.

26. The titanium alloy powder of claim 25, wherein the surface area as determined by BET analysis is at least about 3 square meters per gram after distillation of the powder at temperatures between about 500°C and about 575°C for about 8 to about 12 hours.

27. The titanium alloy powder of claim 25, wherein sodium and calcium and magnesium are present in an amount of less than about 100 ppm.

28. The titanium alloy powder of claim 25, wherein said powder meets ASTM B265 grade 5 chemical specifications.

29. The titanium alloy powder of claim 25, wherein the chloride vapor is introduced at greater than sonic velocity into flowing liquid sodium.

30. The titanium alloy powder of claim 25, wherein the tap density is in the range of from about 4% to about 11%.

31. The titanium alloy powder of claim 25 agglomerated as seen in Figs. 10-12.



32. The titanium alloy powder of claim 29 formed into a sintered product.
33. A solid object made from the titanium alloy powder of claim 29.
34. Agglomerated titanium base alloy powder having about 6% by weight aluminum and about 4% by weight vanadium with an alkali or alkaline earth metal being present in an amount less than about 100 ppm substantially as seen in Figs. 10-12.
35. The titanium alloy powder of claim 34, wherein the surface area as determined by BET analysis is at least about 3 square meters per gram after distillation of the powder at temperatures between about 500°C and about 575°C for about 8 to about 12 hours.
36. The titanium alloy powder of claim 34, wherein said powder meets ASTM B265 grade 5 chemical specifications.
37. The titanium alloy powder of claim 34, wherein the tap density is in the range of from about 4% to about 11.
38. The titanium alloy powder of claim 34 formed into a sintered product.
39. A solid object made from the titanium alloy powder of claim 34.

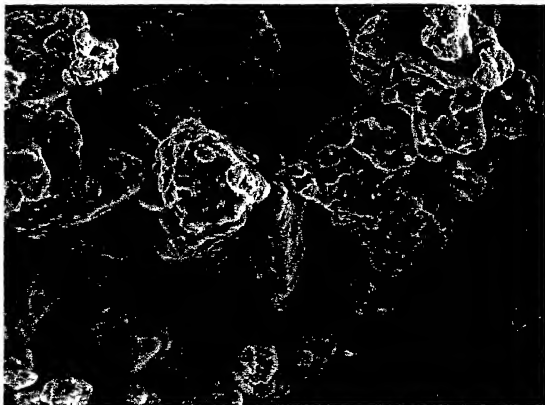


FIGURE 1

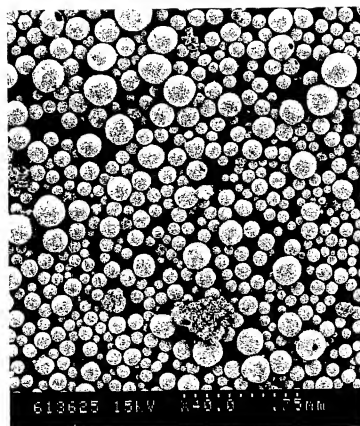
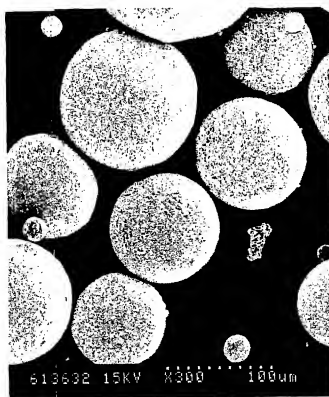


FIGURE 2

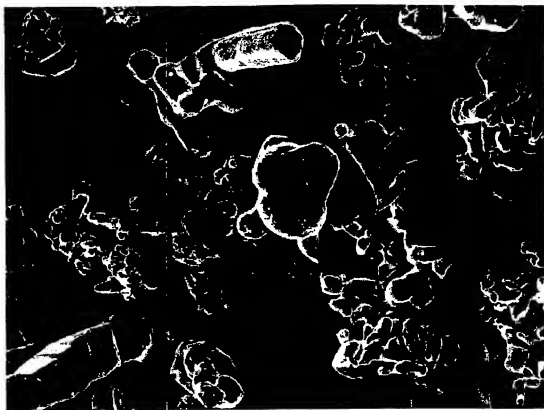


FIGURE 3

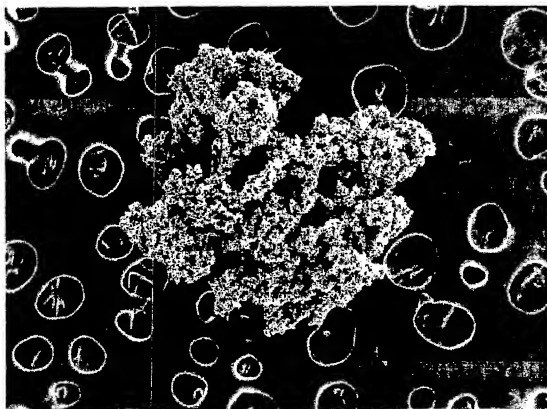


FIGURE 4

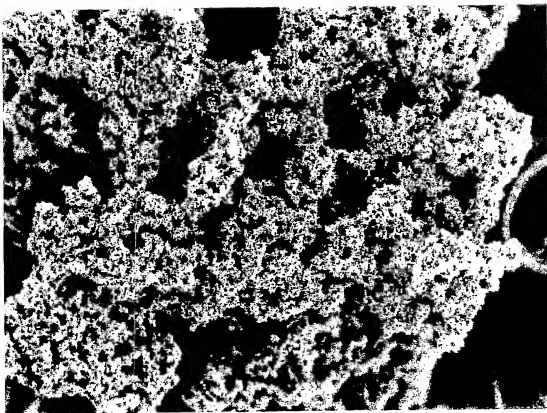


FIGURE 5

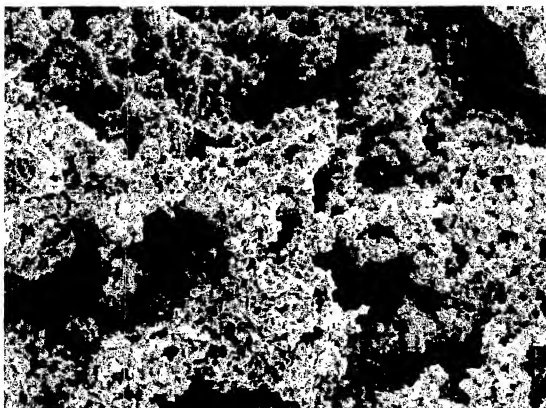


FIGURE 6

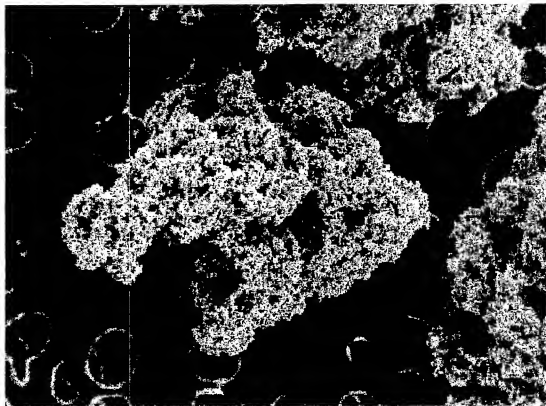


FIGURE 7



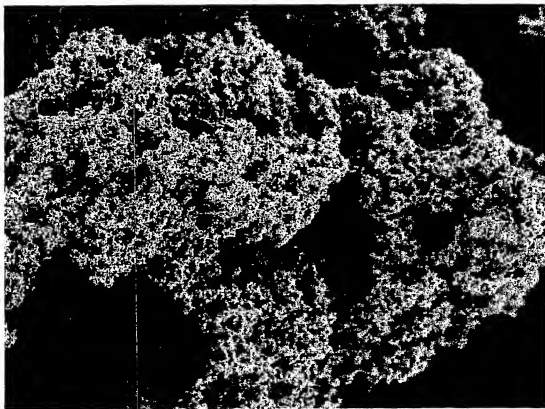


FIGURE 8

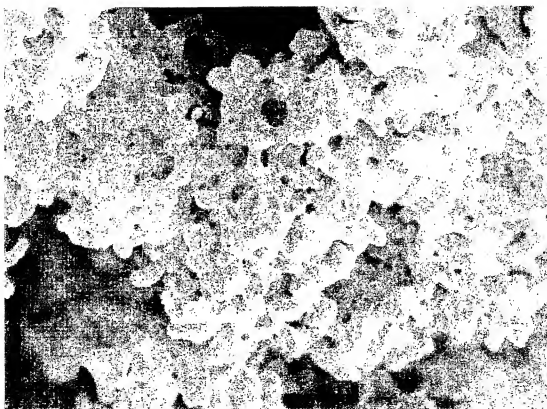


FIGURE 9



FIGURE 10

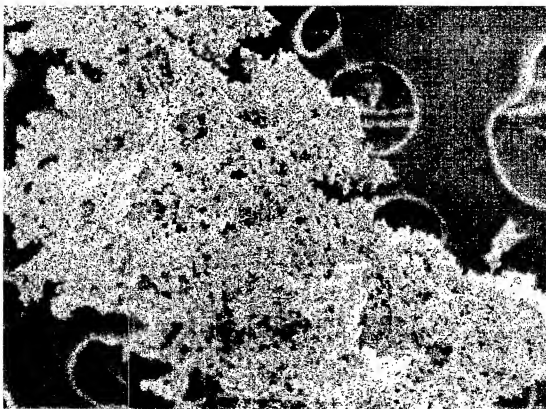


FIGURE 11

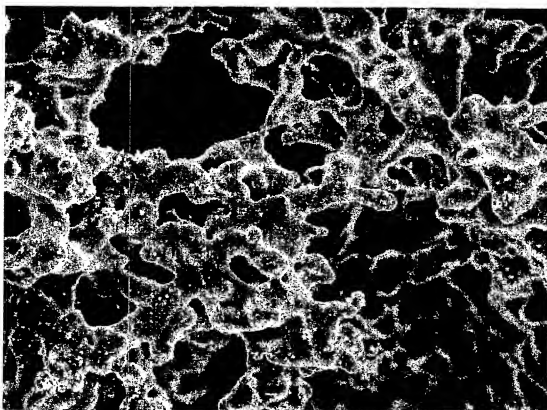


FIGURE 12

## INTERNATIONAL SEARCH REPORT

 International application No  
 PCT/US2006/028396

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> INV. C22B34/12 C22C/04 C22C14/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) C22B C22C		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, COMPENDEX, CHEM ABS Data		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2005/021807 A2 (INTERNAT TITANIUM POWDER LLC [US]; ARMSTRONG DONN REYNOLDS [US]; ANDER) 10 March 2005 (2005-03-10) page 13, last paragraph; claims 10-13	1-39
X	WO 2005/019485 A (INTERNAT TITANIUM POWDER LLC [US]; ERNST WILLIAM A [US]) 3 March 2005 (2005-03-03) page 20, lines 6-10	1-39
X	US 2002/005090 A1 (ARMSTRONG DONN REYNOLDS [US] ET AL) 17 January 2002 (2002-01-17) paragraph [0019]	1-39
-/-		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family		
Date of the actual completion of the international search 21 December 2006		Date of mailing of the international search report 02/01/2007
Name and mailing address of the ISA/ European Patent Office, P.B. 5618 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tlx. 31 651 epo nl, Fax: (+31-70) 340-3015		Authorized officer Badcock, Gordon

## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2006/028396

## C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MAHAJAN, Y. ET AL: "Microstructure Property Correlation in Cold Pressed and Sintered Elemental Ti-6Al-4V Powder Compacts." PUBLISHED BY: TMS/AIME. P.O. BOX 430, 420 COMMONWEALTH DR., WARRENDALE, PA. 15086 CONFERENCE: POWDER METALLURGY OF TITANIUM ALLOYS, LAS VEGAS, NEV., 26-28 FEB. 1980, 1980, XP001248542 experimental	7,8,16, 17,23, 24,33, 34,38,39
A	GERDEMANN, S.J. (ALBANY RESEARCH CENTER (US DOE)) ET AL: "Characterization of a titanium powder produced through a novel continuous process." ADVANCES IN POWDER METALLURGY & PARTICULATE MATERIALS - 2000, PP. 12.41-12.52, GRAPHS, PHOTOMICROGRAPHS, 14 REF. PUBLISHED BY: METAL POWDER INDUSTRIES FEDERATION. 105 COLLEGE RD. EAST, PRINCETON, NJ 08540-6692, USA CONFERENCE: PM2TEC 2000: 2000 INT, 2000, XP001248539 introduction	1-39

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2006/028396

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2005021807 A2	10-03-2005	AU 2004269422 A1 CA 2537659 A1	10-03-2005 10-03-2005
WO 2005019485 A	03-03-2005	NONE	
US 2002005090 A1	17-01-2002	NONE	